



Synthesis, luminescence and gas absorption of a new polythreading coordination polymer



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ABSTRACT

A new compound of $\{[\text{Zn}(\text{btb})(\text{Hbib})] \cdot 2\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}\}_n$ (H_3btb = 1,3,5-benzenetrisbenzoate and bib = 1,4-bis(2-methyl-imidazol-1-yl)butane) was synthesized and characterized. The coordination polymer shows a new (2D $\rightarrow$ 3D) polythreaded array that is obtained from the self-assembly of adjacent 2D layers with dangling lateral arms, in which each large hexagonal void of one layer is threaded by two dangling lateral arms of two adjacent layers belonging to two identical spatial orientations. The luminescence study indicates that the title compound emits bright red fluorescence compared to the free ligand at room temperature. In addition, the small-sized and non-polar pores do not enable **1** to attract CO_2 and N_2 strongly, which can be confirmed by the computational method based on Connolly's algorithm.

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The design and synthesis of porous metal–organic frameworks (MOFs) are now of great interest due to the significance of potential new applications as functional materials [1–3]. Interdigitated networks, as an important subgroup of entangled systems, have provided a long-standing fascination for chemists. With the aid of the rapid growth of network-based crystal engineering, a variety of appealing interdigitated MOFs has been designed and discussed [4–8]. Polythreaded structures are characterized by the presence of closed loops, as well as of elements that can thread through the loops, and can be considered as extended periodic analogs of molecular rotaxanes and pseudorotaxanes [9–12]. However, only a few examples of (2D $\rightarrow$ 3D) interdigitated network assembly from 2D motifs have been reported [9–12].

With this background information, we sought to investigate the role of mixed carboxylate/imidazole framework system. Herein, we have investigated the preparation and structure of material containing the torsionally flexible 1,3,5-benzenetrisbenzoate as an extended trimesic acid analog and flexible imidazole linkage. A new compound of $\{[\text{Zn}(\text{btb})(\text{Hbib})] \cdot 2\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}\}_n$ exhibits a novel (2D $\rightarrow$ 3D) interdigitated architecture that is obtained from the self-assembly of 2D sheet structures. The luminescence study indicates that the title compound emits bright red fluorescence. The gas absorption behavior of **1** has been explored by the computational method based on Connolly's algorithm and experimental confirmation.

Colorless crystals of compound **1** were thermally synthesized by reacting $\text{Zn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, H_3btb and bib and mixed methanol/deionized water solvent at 150 °C for 72 h [13].

The asymmetric unit of **1** contains one Zn atom, one unique btb , one Hbib , two free H_2O molecules and one CH_3OH molecules. Fig. 1a shows the stick view of the local tetrahedral geometry around the Zn(II) atom. The Zn1 is four-coordinated by three O atoms through three monodentate-bridging carboxylate groups from btb ligand and one N atom from bib ligand. Each Zn(II) center is connected by btb ligands to give a 2D rhombic layer with large windows of 15.7×16.5 Å by diagonal (Fig. 1b). Both taking the Zn(II) centers and btb ligands as 3-connecting nodes, the layer can be simplified as the 6^3 net illustrated in Fig. 1c.

The most outstanding feature for **1** is that the structure of **1** displays a new type of (2D $\rightarrow$ 3D) polythreading array assembled by the sidearm-containing 2D layer frameworks, owing to the quite formation of Hbib of threading in this structure. The bib is protonated and is used to balance the full charge. The residual imidazole group of bib fails to coordinate to the Zn1 atom and may act as a dangling arm. Each dangling arm has an effectual length of about 10.19 Å so that one arm is threaded into the windows of two adjacent sheets (Fig. 2a). It is also interesting that each hexagonal void is only penetrated by two bib groups belonging to two different sheets from the same direction (Fig. 2b). So, the 3D polythreading array (2D $\rightarrow$ 3D) can be regarded as the entanglement of five adjacent polymeric layers at a time (Fig. 2c). To our knowledge, of the previously reported interdigitated examples, almost all are related to highly undulating layers containing small and cramped windows or layers involving protrudent side arms [10–12]. Therefore, this type of

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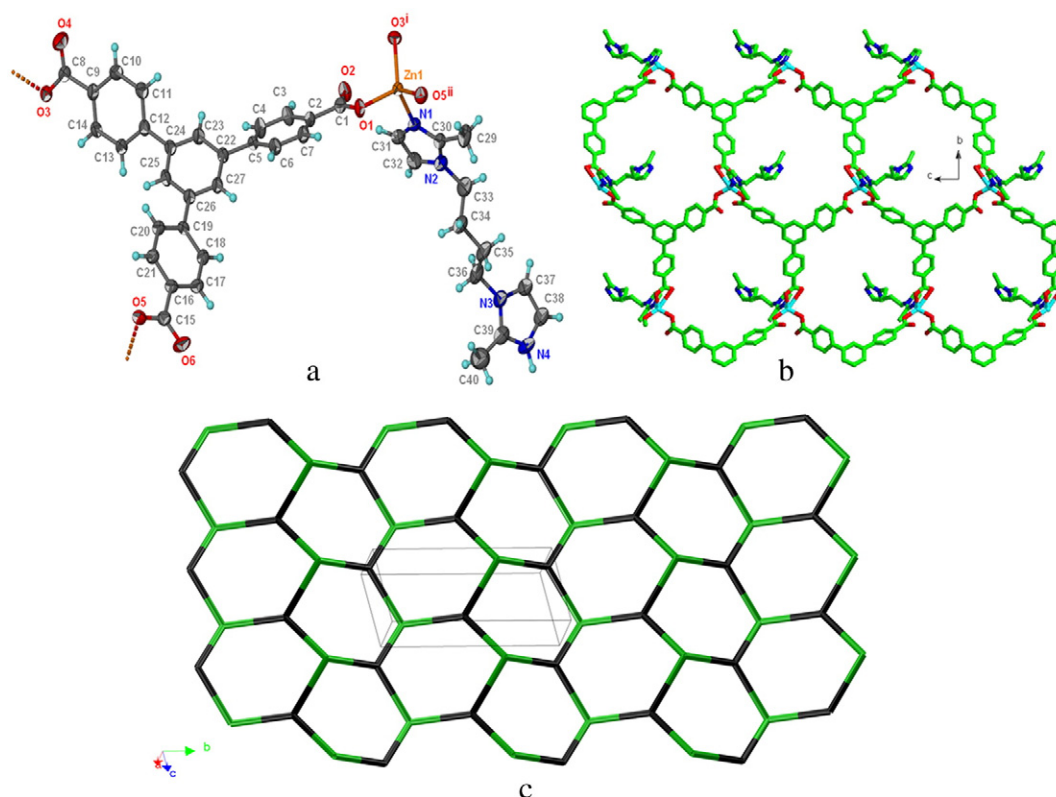


Fig. 1. (a) The coordination geometries of the metal centers and the ligand geometries in compound **1** (symmetric codes: (i) $-x, 1/2 + y, 1/2 - z$; (ii) $-x, -y, -z$); (b) the 2D honeycomb-like layer; (c) the 6³ topological net (the cyan node represents Zn center and the black node represents organic linker).

polythreaded architecture in **1**, assembled from 2D sheet structure, is especially rare in entangled systems [14]. As far as we know, a 3D polythreading structure based on 2D layer motifs was firstly observed in a zinc coordination polymer reported by Wang et al. [14f]. Latterly, they also find a new type of unusual (2D $\rightarrow$ 3D) polythreading array based on 2D (4,4) layers with dangling ligands, which exhibit a unique

simultaneous threading fashion of five adjacent polymeric motifs [14g]. Then, more and more (2D $\rightarrow$ 3D) polythreading examples were documented by others. For example, an 8-connected entangled MOF with co-existence of self-threading polythreading and interpenetration has been constructed by Co(II) and trigonal ligand 4-([4,2':6',4''-terpyridin]-4'-yl) benzoic acid [14b]. Zhang and his co-workers reported that parallel

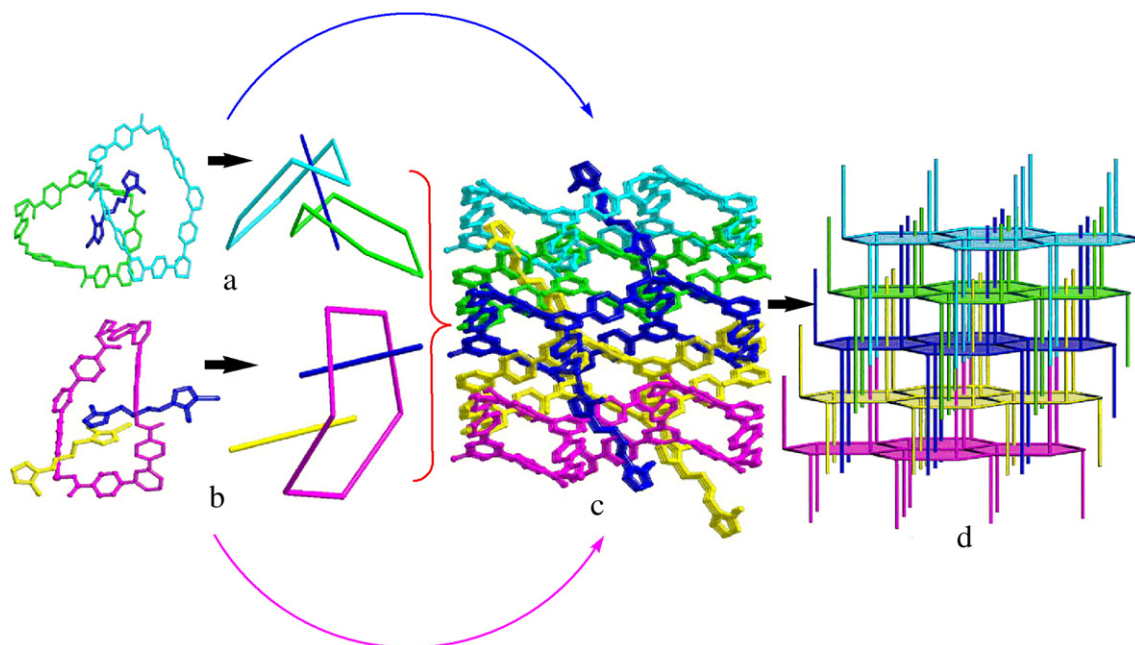


Fig. 2. (a) Perspective view of the dangling arms of bib thread two adjacent layers; (b) view of the hexagonal voids is threaded by two dangling arms from two adjacent layers at the same direction; (c) view of the polythreaded array (2D $\rightarrow$ 3D) of five adjacent polymeric layers at a time. (d) Schematic view of the (2D $\rightarrow$ 3D) interdigitated array of **1**.

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